Monoclinic Double Selenates of the Cobalt Group.

By A. E. H. TUTTON, D.Sc., M.A., F.R.S.

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This memoir deals with the four double selenates of the series $R_2M(SeO_4)_2 \cdot 6H_2O$, in which M is cobalt and R is potassium, rubidium, cæsium, and ammonium. Only the potassium and ammonium salts of this cobalt group have been hitherto investigated. They were prepared and analysed by von Hauer,* the crystals measured by Haldor Topsøe,† and their optical properties partially determined by Topsøe and Christiansen.‡ The salts were prepared for this present investigation by dissolving pure cobalt carbonate in the calculated quantity of dilute selenic acid, boiling off carbon dioxide, and filtering; then adding the solution of cobalt selenate so obtained to a molecularly equivalent quantity of a solution of the alkali selenate, one drop excess of selenic acid being eventually added to the mixed solution to ensure perfect clarity. The ammonium and potassium selenates were from a very pure stock prepared in some quantity a short time ago; the rubidium and cæsium selenates were freshly prepared by dissolving the pure carbonates in selenic acid, and boiling off carbon dioxide. The crystallisations were effected from metastable solutions, with all the precautions previously described, and numerous crops of the beautiful ruby red crystals of all four salts were obtained, of which several in each case proved suitable for the measurements and determinations.

The work on these four salts is especially similar and parallel to that on the four analogous nickel salts described in 1916,§ so that descriptions of methods need not be again given, but merely the results communicated.

Potassium Cobalt Selenate, $K_2Co(SeO_4)_2 \,.\, 6H_2O$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 104° \, 17'$. Topsøe's value 104° 10′.

Ratio of Axes.—$a : b : c = 0{\cdot}7522 : 1 : 0{\cdot}5062$.

Topsøe's value $0{\cdot}7379 : 1 : 0{\cdot}5056$.

Forms observed.—$a\{100\}$, $b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $r'\{\bar{2}01\}$. The forms a and p' were not observed by Topsøe.

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* 'Wien. Akad. Sitzber.,' vol. 39, p. 839 (1860).

† 'Krystallogr.-kem. Unders. o. de Selensure Salte,' Copenhagen, 1870.

‡ 'Ann. de Chim. et de Phys.,' Ser. 5, vol. 1, pp. 78 and 79 (1874).

§ 'Phil. Trans.,' A, vol. 217, p. 199 (1917).

Interfacial Angles of Potassium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Values of Topsøe.
		° ′ ° ′	° ′	° ′	′	° ′
$ac = (100) : (001)$...	3	75 45– 75 51	75 47	75 43	4	
$as = (100) : (101)$...	—	—	—	46 27	—	
$sc = (101) : (001)$...	—	—	—	29 16	—	
$cr' = (001) : (\bar{2}01)$...	12	62 53– 63 14	63 7	62 58	9	63 21
$cs' = (001) : (\bar{1}01)$...	—	—	—	38 6	—	
$s'r' = (\bar{1}01) : (\bar{2}01)$...	—	—	—	24 52	—	
$r'a = (\bar{2}01) : (\bar{1}00)$...	2	41 8– 41 10	41 9	41 19	10	
$r'c = (\bar{2}01) : (00\bar{1})$...	14	116 39–117 37	116 52	117 2	10	117 3
$ap = (100) : (110)$...	6	35 51– 36 6	36 0	36 3	3	
$pp' = (110) : (120)$...	1	—	19 25	19 28	3	
$p'b = (120) : (010)$...	—	—	—	34 29	—	
$pp''' = (110) : (130)$...	—	—	—	29 21	—	
$p'''b = (130) : (010)$...	—	—	—	24 36	—	
$pb = (110) : (010)$...	2	53 47– 54 3	53 55	53 57	2	
$pp = (110) : (1\bar{1}0)$...	21	71 50– 72 21	72 7	*	—	71 10
$pp = (110) : (\bar{1}10)$...	20	107 38–108 1	107 52	107 53	1	108 43
$cq = (001) : (011)$...	39	25 56– 26 14	26 8	*	—	26 7
$qb = (011) : (010)$...	6	63 36– 64 1	63 48	63 52	4	
$qq = (011) : (01\bar{1})$...	19	127 35–127 55	127 45	127 44	1	
$ao = (100) : (111)$...	—	—	—	49 42	—	
$oq = (111) : (011)$...	—	—	—	27 31	—	
$aq = (100) : (011)$...	—	—	—	77 13	—	
$qo' = (011) : (\bar{1}11)$...	—	—	—	34 15	—	
$o'a = (\bar{1}11) : (\bar{1}00)$...	—	—	—	68 32	—	
$co = (001) : (111)$...	—	—	—	35 1	—	
$op = (111) : (110)$...	—	—	—	43 29	—	
$cp = (001) : (110)$...	40	78 21– 78 41	78 30	*	—	78 21
$po' = (110) : (11\bar{1})$...	—	—	—	57 6	—	
$o'c = (11\bar{1}) : (00\bar{1})$...	—	—	—	44 24	—	
$pc = (110) : (00\bar{1})$...	40	101 16–101 38	101 29	101 30	1	101 29
$bn = (010) : (121)$...	—	—	—	53 44	—	
$no = (121) : (111)$...	—	—	—	16 7	—	
$bo = (010) : (111)$...	—	—	—	69 51	—	
$os = (111) : (101)$...	—	—	—	20 9	—	
$bo' = (010) : (\bar{1}11)$...	—	—	—	65 9	—	
$o's' = (\bar{1}11) : (\bar{1}01)$...	—	—	—	24 51	—	
$o'o' = (\bar{1}11) : (\bar{1}\bar{1}1)$...	—	—	—	49 42	—	
$sq = (101) : (011)$...	—	—	—	38 27	—	
$qp = (011) : (\bar{1}10)$...	36	85 11– 85 39	85 22	85 24	2	85 33
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$...	—	—	—	56 9	—	
$pq = (\bar{1}10) : (0\bar{1}\bar{1})$...	36	94 15– 94 52	94 38	94 36	2	
$s'q = (\bar{1}01) : (011)$...	—	—	—	45 3	—	
$qn = (011) : (121)$...	—	—	—	26 52	—	
$np = (121) : (110)$...	—	—	—	37 8	—	
$qp = (011) : (110)$...	38	63 47– 64 17	64 2	64 0	2	64 16
$ps' = (110) : (10\bar{1})$...	—	—	—	70 57	—	
$pq = (110) : (0\bar{1}\bar{1})$...	38	115 42–116 13	115 58	116 0	2	
$r'o' = (\bar{2}01) : (\bar{1}11)$...	—	—	—	34 35	—	
$o'p = (\bar{1}11) : (110)$...	—	—	—	92 48	—	
$pr' = (110) : (20\bar{1})$...	18	52 23– 52 38	52 28	52 37	9	51 58
$r'p = (\bar{2}01) : (110)$...	16	127 24–127 38	127 30	127 23	7	
Total number of measurements from 10 crystals	407					

Habit.—That characteristic of the potassium salts of the series, namely, short prismatic parallel to the vertical axis *c*, to tabular parallel to *c*{001}, with *c*{001} and *p*{110} vastly predominating, *q*{011} being very small. A typical crystal is represented in fig. 1.

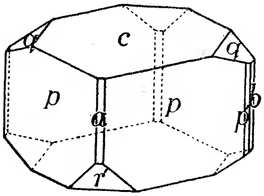

Fig. 1.

The very small faces of *r'*{$\bar{2}$01} were usually the only other faces visible, but on two measured crystals narrow strip-faces of *a*{100} and *b*{010} were present. One good little face of the prism *p'*{120} was present on one of the measured crystals. The *p*-faces of this salt were generally more affected by striation than those of the other salts of the group, and more difficulty was experienced, but eventually overcome, in finding ten crystals adequately free from this fault. The crystal measured by Topsøe was obviously much affected by striation, his value for the angle *pp* = (110) : (1$\bar{1}$0) being much too small.

Cleavage.—Excellent parallel to *r'*{$\bar{2}$01}.

Relative Density.—Six determinations were made by the immersion method using methylene iodide and benzene mixture.

I.	Density for	18°·4/4°	2·5292	For 20°/4°	2·5288
II.	„	18°·2/4°	2·5310	„	2·5305
III.	„	18°·3/4°	2·5308	„	2·5304
IV.	„	18°·0/4°	2·5300	„	2·5295
V.	„	18°·3/4°	2·5291	„	2·5287
VI.	„	18°·9/4°	2·5292	„	2·5289
				Mean	2·5295

Accepted value for 20°/4°.........**2·530.**

Molecular Volume.—$\frac{M}{d} = \frac{527{\cdot}77}{2{\cdot}530} = 208{\cdot}60$.

Topsøe found the specific gravity 2·514, a value much too low, and the molecular volume correspondingly much too high, 211·5.

Molecular Distance Ratios (topic axial ratios).—

$$\chi : \psi : \omega = 6{\cdot}2197 : 8{\cdot}2688 : 4{\cdot}1856.$$

Orientation of Optical Ellipsoid.—Plane of optic axes *b*{010}. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and the second median line is α.

Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I......5° 21′, Plate II......5° 25′, Mean......5° 23′,

behind the normal to *c* (001). As the latter is 14° 17′ in front of the vertical axis *c*, the second median line lies 8° 54′ in front of the vertical axis *c*. The first median line lies 5° 23′ above the inclined axis *a*. Topsøe and Christiansen found 3° 25′ for the latter. Fig. 2 will render these facts clear.

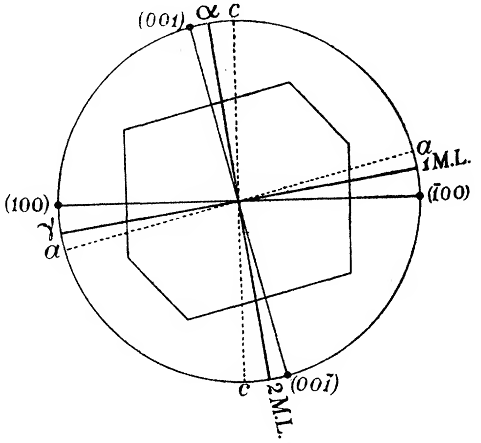

Fig. 2.

Optic Axial Angle.—Results with three pairs of plates ground perpendicular to the first and second median lines. Plate 3 was so thick and therefore absorptive, that 2E was not clearly measurable with it.

Apparent Optic Axial Angle in Air, 2E, of KCo Selenate.

Light.	Plate 1.	Plate 2.	Mean 2E.
	° ′	° ′	° ′
Li.................	103 51	103 34	103 43
C	103 58	103 40	103 49
Na	104 28	104 21	104 25
Tl.................	105 12	105 23	105 18
Cd	105 38	105 53	105 46

Topsøe and Christiansen obtained 106° 58′ for 2E for sodium light.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	56 34	1*a*	103 44	62 7	62 12
	2	56 40	2*a*	103 31	62 17	
	3	56 37	3*a*	103 40	62 11	
C	1	56 34	1*a*	103 41	62 8	62 13
	2	56 40	2*a*	103 28	62 18	
	3	56 37	3*a*	103 38	62 12	
Na	1	56 30	1*a*	103 17	62 14	62 19
	2	56 36	2*a*	103 2	62 24	
	3	56 33	3*a*	103 7	62 20	
Tl	1	56 24	1*a*	102 52	62 18	62 27
	2	56 32	2*a*	102 24	62 34	
	3	56 28	3*a*	102 29	62 29	

Owing to the strong absorption by these ruby-red crystals of light of wave-lengths beyond that of the thallium green line, the true optic axial angle could only be determined by observations of $2H_a$ and $2H_o$ in bromonaphthalene so far as for that colour. In the case of 2E, observations were found possible as far as the wave-length of the green cadmium line.

Topsøe and Christiansen found 63° 52′ for $2V_a$ for sodium light.

Dispersion of the Median Lines.—This was determined by immersion in monochlorbenzene, the refractive index of which, 1·5248 for Na light, is almost absolutely identical with the mean index of the crystals, 1·5252 for Na light. It proved to be exceedingly small, less than 5′, and the brushes showed no colour at all on their margins (except the pale red of the section itself).

Effect of Temperature on Optic Axial Angle.—2E was determined with section 1 for 80° C., and found to be 110° 6′ for Na light. Hence the angle in air increases 5½° on heating from the ordinary temperature to 80° C.

Refractive Indices.—Results with six 60°-prisms, each ground to yield two indices. The images were clearly discernible even for Cd, F, and G light.

Refractive Indices of Potassium Cobalt Selenate.

Light.	α.	β.	γ.
Li	1·5122	1·5181	1·5341
C	1·5127	1·5186	1·5347
Na	1·5158	1·5218	1·5380
Tl	1·5190	1·5250	1·5415
Cd	1·5211	1·5271	1·5435
F	1·5231	1·5291	1·5456
G	1·5293	1·5354	1·5522

Mean of α, β, and γ for Na light = 1·5252.

α = Vibration direction parallel to second median line, 8° 54′ in front of axis *c*.
β = „ „ „ symmetry axis *b*.
γ = „ „ „ first median line, 5° 23′ above axis *a*.

Double refraction, $Na_{\gamma-\alpha} = 0·0222$.

General formula for β, corrected to a vacuum:—

$$\beta = 1{\cdot}5026 + \frac{813\ 127}{\lambda^2} - \frac{4\ 606\ 800\ 000\ 000}{\lambda^4} + \ldots.$$

The α indices are equally well reproduced by the formula if the constant 1·5026 be diminished by 0·0060, and the γ indices if it be increased by 0·0163.

Observations at 70° indicated that the refractive indices diminish by about 0·0026 for a rise of 60° of temperature.

The values of Topsøe and Christiansen were: for β, line C 1·5162, line D 1·5195, line F 1·5270; the α and γ values were only obtained indirectly and for line D only; they are given as 1·5135 and 1·5358.

Axial Ratios of the Optical Ellipsoid—

$$\alpha : \beta ; \gamma = 0{\cdot}9960 : 1 : 1{\cdot}0106, \qquad \mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0040 : 1 : 0{\cdot}9895.$$

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.........	C	0·1187	0·1199	0·1230
		G	0·1220	0·1231	0·1263
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$.	C	62·66	63·27	64·91
		G	64·36	64·98	66·68
	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0033	0·0032	0·0033
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·70	1·71	1·77
Gladstone...	Molecular refraction, $\frac{n-1}{d}$ M	C	106·95	108·18	111·54

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha + \beta + \gamma) = 108{\cdot}89$.

Rubidium Cobalt Selenate, $Rb_2Co(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 105° 14'$.

Ratio of Axes.—$a : \breve{b} : c = 0{\cdot}7427 : 1 : 0{\cdot}5019$.

Forms observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o'\{\bar{1}11\}$.

Habit.—More or less tabular parallel to $c\ \{001\}$, to short prismatic parallel to the vertical axis c as prism axis. The greater portion of the numerous crops obtained were of the former type; a typical specimen is shown in fig. 3

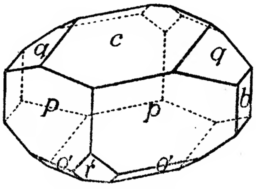

FIG. 3.

Interfacial Angles of Rubidium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
		° ′ ° ′	° ′	° ′	′
$ac = (100):(001)$......	—	—	—	74 46	
$as = (100):(101)$......	—	—	—	45 48	
$sc = (101):(001)$......	—	—	—	28 58	
$cr' = (001):(\bar{2}01)$......	15	63 41- 63 58	63 48	63 43	5
$cs' = (001):(\bar{1}01)$......	—	—	—	38 25	
$s'r' = (\bar{1}01):(\bar{2}01)$......	—	—	—	25 18	
$r'a = (\bar{2}01):(\bar{1}00)$......	—	—	—	41 31	
$r'c = (\bar{2}01):(00\bar{1})$......	15	116 2-116 19	116 12	116 17	5
$ap = (100):(110)$......	—	—	—	35 38	
$pp' = (110):(120)$......	—	—	—	19 28	
$p'b = (120):(010)$......	—	—	—	34 54	
$pp''' = (110):(130)$......	—	—	—	29 26	
$p'''b = (130):(010)$......	—	—	—	24 56	
$pb = (110):(010)$......	37	54 15- 54 31	54 22	*	
$pp = (110):(1\bar{1}0)$......	21	71 8- 71 29	71 16	71 16	0
$pp = (110):(\bar{1}10)$......	22	108 24-108 52	108 43	108 44	1
$cq = (001):(011)$......	39	25 34- 25 58	25 50	*	
$qb = (011):(010)$......	36	64 3- 64 30	64 10	64 10	0
$qq = (011):(01\bar{1})$......	20	128 6-128 37	128 20	128 20	0
$ao = (100):(111)$......	—	—	—	49 0	
$oq = (111):(011)$......	—	—	—	27 19	
$aq = (100):(011)$......	—	—	—	76 19	
$qo' = (011):(\bar{1}11)$......	—	—	—	34 37	
$o'a = (\bar{1}11):(\bar{1}00)$......	—	—	—	69 4	
$co = (001):(111)$......	—	—	—	34 35	
$op = (111):(110)$......	—	—	—	43 5	
$cp = (001):(110)$......	40	77 33- 77 47	77 40	*	
$po' = (110):(11\bar{1})$......	11	57 23- 57 46	57 37	57 42	5
$o'c = (11\bar{1}):(00\bar{1})$......	11	44 34- 44 52	44 41	44 38	3
$pc = (110):(00\bar{1})$......	40	102 10-102 27	102 19	102 20	1
$bn = (010):(121)$......	—	—	—	54 16	
$no = (121):(111)$......	—	—	—	15 57	
$bo = (010):(111)$......	—	—	—	70 13	
$os = (111):(101)$......	—	—	—	19 47	
$bo' = (010):(\bar{1}11)$......	9	65 8- 65 18	65 13	65 14	1
$o's' = (\bar{1}11):(\bar{1}01)$......	—	—	—	24 46	
$o'o' = (\bar{1}11):(\bar{1}\bar{1}1)$......	4	49 28- 49 41	49 34	49 32	2
$sq = (101):(011)$......	—	—	—	38 3	
$qp = (011):(\bar{1}10)$......	35	86 14- 86 46	86 29	86 28	1
$ps = (\bar{1}10):(\bar{1}0\bar{1})$......	—	—	—	55 29	
$pq = (\bar{1}10):(0\bar{1}\bar{1})$......	35	93 16- 93 46	93 31	93 32	1
$s'q = (\bar{1}01):(011)$......	—	—	—	45 9	
$qn = (011):(121)$......	—	—	—	26 39	
$np = (121):(110)$......	—	—	—	36 51	
$qp = (011):(110)$......	36	63 21- 63 46	63 32	63 30	2
$ps' = (110):(10\bar{1})$......	—	—	—	71 21	
$pq = (110):(0\bar{1}\bar{1})$......	36	116 15-116 42	116 28	116 30	2
$r'o' = (\bar{2}01):(\bar{1}11)$......	12	34 39- 35 0	34 51	34 49	2
$o'p = (\bar{1}11):(110)$......	12	92 35- 92 58	92 45	92 40	5
$pr' = (110):(20\bar{1})$......	32	52 15- 52 32	52 24	52 31	7
$r'p = (\bar{2}01):(110)$......	32	127 29-127 44	127 36	127 29	7
Total number of measurements from 10 crystals	550				

The *q*-faces were relatively larger, compared with the *c*-faces, than in the case of the potassium salt, but the *c*-faces in most cases still predominated as the principal faces of the tablet.

The *p*-faces were always important, and their lesser or greater depth determined the tabular or prismatic character of the crystals.

The faces of *r′* were almost invariably small, and those of *o′* were but narrow strips modifying the *cp* edges. The clinopinakoid faces *b* were also small, but usually gave excellent reflections of the signal. Ten excellent crystals were measured.

Cleavage.—Parallel to $r'\{\bar{2}01\}$, perfect.

Relative Density.—Six determinations were made by the immersion method.

I.	Density for	16°·8/4°	2·8367	For 20°/4°	2·8358
II.	„	17°·9/4°	2·8368	„	2·8362
III.	„	18°·2/4°	2·8390	„	2·8385
IV.	„	17°·3/4°	2·8379	„	2·8371
V.	„	18°·8/4°	2·8375	„	2·8372
VI.	„	18°·4/4°	2·8385	„	2·8380
				Mean	2·8371

Accepted value for 20°/4°......**2·837**.

Molecular Volume.—$\frac{M}{d} = \frac{619{\cdot}87}{2{\cdot}837} = 218{\cdot}49$.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6{\cdot}2901 : 8{\cdot}4693 : 4{\cdot}2508.$$

Orientation of Optical Ellipsoid.—Plane of optic axes, $b\{010\}$. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and the second median line is α.

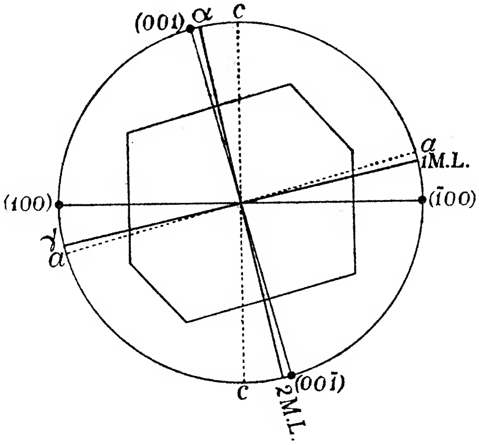

Fig. 4.

Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I...1° 24′, Plate II...3° 2′. Plate III...2° 45′, Mean...2° 24′,

behind the normal to $c(001)$. As that normal is 15° 14′ in front of the vertical axis c, the second median line lies 12° 50′ in front of the vertical axis c. The first median line lies 2° 24′ above the inclined axis a. Fig. 4 will render this clear.

Optic Axial Angle.—Results with three pairs of section-plates perpendicular to the two median lines. Plate 2 did not quite admit of 2E being fully visible, being narrow and the angle in air very wide.

Apparent Optic Axial Angle in Air, 2E, of RbCo Selenate.

Light.	Plate 1.	Plate 3.	Mean 2E.
	° ′	° ′	° ′
Li................	131 40	130 35	131 8
C	131 48	130 40	131 14
Na	132 40	131 30	132 5
Tl	133 30	132 30	133 0

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li.........	1	66 56	1*a*	94 40	73 44	73 42
	2	67 9	2*a*	94 38	73 54	
	3	66 26	3*a*	94 28	73 28	
C	1	66 53	1*a*	94 35	73 44	73 41
	2	67 5	2*a*	94 35	73 53	
	3	66 22	3*a*	94 24	73 26	
Na	1	66 34	1*a*	94 11	73 41	73 37
	2	66 46	2*a*	94 15	73 47	
	3	66 3	3*a*	94 2	73 22	
Tl.........	1	66 15	1*a*	93 47	73 38	73 33
	2	66 27	2*a*	93 53	73 40	
	3	65 46	3*a*	93 36	73 20	

The absorption by these ruby red crystals did not admit of accurate measurements beyond the green.

Dispersion of the Median Lines.—This was determined by immersion of the sections perpendicular to the first median line in monochlorbenzene, the refractive index of which is almost identical with the mean index of the crystals. The dispersion proved to be exceedingly small, less than 5′, so small, indeed, that its direction was not determinable with certainty. The vertices of the brushes were quite black, as seen in this liquid, with no perceptible colour at the margins except the natural red of the section-plates themselves.

Effect of Temperature on Optic Axial Angle.—Determinations of 2E at 75° C. indicated that the angle in air increases 5° on raising the temperature 65° from the ordinary temperature to 75° C.

Refractive Indices.—Results obtained with six 60°-prisms, each ground to afford two indices directly.

Refractive Indices of Rubidium Cobalt Selenate.

Light.	α.	β.	γ.
Li.................	1·5163	1·5220	1·5329
C	1·5168	1·5225	1·5334
Na	1·5199	1·5256	1·5369
Tl.................	1·5232	1·5290	1·5404
Cd	1·5252	1·5311	1·5425
F	1·5273	1·5332	1·5446
G	1·5333	1·5393	1·5508

Mean of α, β, and γ for Na light = 1·5275.

α = Vibration direction parallel to second median line, 12° 50′ in front of axis c.
β = " " " symmetry axis b.
γ = " " " first median line, 2° 24′ above axis a.

Double refraction, $\mathrm{Na}_{\gamma-\alpha}$ = 0·0170.

General formula β, corrected to a vacuum:—

$$\beta = 1{\cdot}5098 + \frac{571\ 580}{\lambda^2} - \frac{316\ 900\ 000\ 000}{\lambda^4} + \ldots .$$

The α indices are also reproduced by the formula if the constant 1·5098 be diminished by 0·0057, and the γ indices if it be increased by 0·0113.

Observations at 70° indicated that the refractive indices diminish with rise of temperature, to the extent of 0·0025 for 60° rise of temperature.

Axial Ratios of the Optical Ellipsoid—

$$\alpha : \beta : \gamma = 0{\cdot}9963 : 1 : 1{\cdot}0074, \qquad \mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0037 : 1 : 0{\cdot}9926.$$

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$.........	C	0·1066	0·1076	0·1095
		G	0·1094	0·1105	0·1124
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$...	C	66·08	66·69	67·86
		G	67·84	68·48	69·69
	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$		0·0028	0·0029	0·0029
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$		1·76	1·79	1·83
Gladstone ...	Molecular refraction, $\frac{n-1}{d}M$	C	112·92	114·16	116·54

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha + \beta + \gamma)$ = 114·54.

Cæsium Cobalt Selenate, $Cs_2Co(SeO_4)_2 \cdot 6H_2O$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 106° 18'$.

Ratio of Axes.—$a : b : c = 0·7310 : 1 : 0·4989$.

Forms observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $q\{011\}$, $r'\{\bar{2}01\}$, $o'\{\bar{1}11\}$.

Habit.—Prismatic parallel to inclined axis a. A typical crystal is shown in fig. 5.

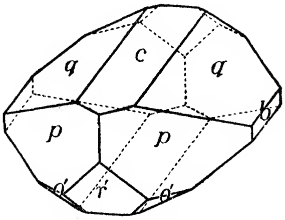

Fig. 5.

The characteristics of the cæsium salts of this grand series are well shown by cæsium cobalt selenate, namely, narrow $c\{001\}$ faces and broader $q\{011\}$ faces. The great majority of the crystals showed no faces of either $b\{010\}$ or $o'\{\bar{1}11)$, and not infrequently also no $r'\{\bar{2}01\}$ faces, the only forms developed being $c\{001\}$, $q\{011\}$, and $p\{110\}$. Occasionally an excellent face of $b\{010\}$ was found on the larger crystals.

Cleavage.—Perfect parallel $r'\{\bar{2}01\}$.

Relative Density.—Six determinations were carried out by the immersion method.

I.	Density for 19°·2/4° ……	3·0938	For 20°/4° ……	3·0936
II.	,, 17°·9/4° ……	3·0939	,, ……	3·0933
III.	,, 17°·9/4° ……	3·0924	,, ……	3·0918
IV.	,, 18°·9/4° ……	3·0958	,, ……	3·0955
V.	,, 16°·7/4° ……	3·0954	,, ……	3·0944
VI.	,, 17°·2/4° ……	3·0947	,, ……	3·0938
			Mean ……	3·0937

Accepted value for 20°/4°……**3·094**.

Molecular Volume.—$\frac{M}{d} = \frac{713·87}{3·094} = 230·73$.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6·3618 : 8·7028 : 4·3418.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction positive. The first median line is the γ axis of the indicatrix, and the second line median is α.

Interfacial Angles of Cæsium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.
		° ′ ° ′	° ′	° ′	′
$ac = (100) : (001)$......	—	—	—	73 42	
$as = (100) : (101)$......	—	—	—	44 55	
$sc = (101) : (001)$......	—	—	—	28 47	
$cr' = (001) : (\bar{2}01)$......	15	64 31– 64 59	64 48	64 46	2
$cs' = (001) : (\bar{1}01)$......	—	—	—	39 0	
$s'r' = (\bar{1}01) : (\bar{2}01)$......	—	—	—	25 46	
$r'a = (\bar{2}01) : (\bar{1}00)$......	—	—	—	41 32	
$r'c = (\bar{2}01) : (00\bar{1})$......	15	115 3–115 33	115 13	115 14	1
$ap = (100) : (110)$......	—	—	—	35 3·5	
$pp' = (110) : (120)$......	—	—	—	19 28	
$p'b = (120) : (010)$......	—	—	—	35 28	
$pp''' = (110) : (130)$......	—	—	—	29 31	
$p'''b = (130) : (010)$......	—	—	—	25 25	
$pb = (110) : (010)$......	4	54 56– 54 59	54 58	54 56·5	1·5
$pp = (110) : (1\bar{1}0)$......	22	69 53– 70 20	70 7	*	
$pp = (110) : (\bar{1}\bar{1}0)$......	22	109 43–110 18	109 53	109 53	0
$cq = (001) : (011)$......	43	25 26– 25 48	25 35	*	
$qb = (011) : (010)$......	8	64 23– 64 26	64 24	64 25	1
$qq = (011) : (01\bar{1})$......	21	128 41–128 54	128 49	128 50	1
$ao = (100) : (111)$......	—	—	—	48 6	
$oq = (111) : (011)$......	—	—	—	27 14	
$aq = (100) : (011)$......	—	—	—	75 20	
$qo' = (011) : (\bar{1}11)$......	—	—	—	35 12	
$o'a = (\bar{1}11) : (\bar{1}00)$......	—	—	—	69 28	
$co = (001) : (111)$......	—	—	—	34 14	
$op = (111) : (110)$......	—	—	—	42 29	
$cp = (001) : (110)$......	42	76 32– 76 52	76 43	*	
$po' = (110) : (11\bar{1})$......	7	58 0– 58 18	58 8	58 10	2
$o'c = (11\bar{1}) : (00\bar{1})$......	11	44 58– 45 18	45 11	45 7	4
$pc = (110) : (00\bar{1})$......	42	103 8–103 27	103 16	103 17	1
$bn = (010) : (121)$......	—	—	—	54 51	
$no = (121) : (111)$......	—	—	—	15 45	
$bo = (010) : (111)$......	—	—	—	70 36	
$os = (111) : (101)$......	—	—	—	19 24	
$bo' = (010) : (\bar{1}11)$......	6	65 17– 65 24	65 21	65 17	4
$o's' = (\bar{1}11) : (\bar{1}01)$......	—	—	—	24 43	
$o'o' = (\bar{1}11) : (\bar{1}\bar{1}1)$......	6	49 13– 49 26	49 22	49 26	4
$sq = (101) : (011)$......	—	—	—	37 46	
$qp = (011) : (\bar{1}10)$......	43	87 34– 87 52	87 42	87 40	2
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$......	—	—	—	54 34	
$pq = (\bar{1}10) : (0\bar{1}\bar{1})$......	43	92 6– 92 26	92 18	92 20	2
$s'q = (\bar{1}01) : (011)$......	—	—	—	45 30	
$qn = (011) : (121)$......	—	—	—	26 30	
$np = (121) : (110)$......	—	—	—	36 25	
$qp = (011) : (110)$......	42	62 42– 63 17	62 55	62 55	0
$ps' = (110) : (10\bar{1})$......	—	—	—	71 35	
$pq = (110) : (0\bar{1}\bar{1})$......	41	116 48–117 17	117 5	117 5	0
$r'o' = (\bar{2}01) : (\bar{1}11)$......	10	34 55– 35 18	35 8	35 7	1
$o'p = (\bar{1}11) : (110)$......	9	92 35– 92 44	92 39	92 40	1
$pr' = (110) : (20\bar{1})$......	21	52 1– 52 20	52 14	52 13	1
$r'p = (\bar{2}01) : (110)$......	21	127 38–127 57	127 46	127 47	1
Total number of measurements from 11 crystals	494				

Extinction Direction (2 M.L.) in Symmetry Plane.

Plate I......2° 40′, Plate II......3° 13′, Plate III......3° 21,
Mean extinction angle......3° 5′,

in front of the normal to *c*(001). As that normal is already 16° 18′ in front of the vertical axis *c*, the second median line lies 19° 23′ in front of the vertical axis *c*. The first median line lies 3° 5′ below the inclined axis *a*. Fig. 6 will render the position plain.

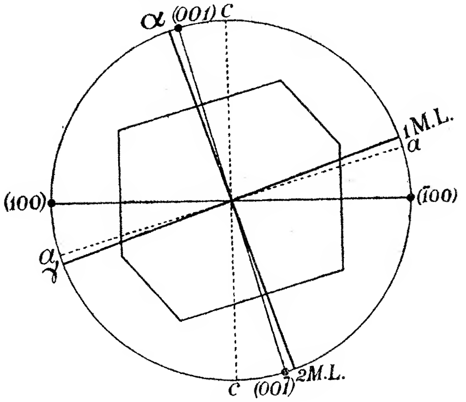

Fig. 6.

Optic Axial Angle.—Results for three pairs of section-plates, ground perpendicular to the two median lines. The optic axial angle is so large that it does not emerge in air.

Cæsium Cobalt Selenate.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	°
Li.........	1	79 16	1*a*	84 16	87 7	87 11
	2	79 20	2*a*	84 21	87 6	
	3	79 34	3*a*	84 13	87 20	
C	1	79 10	1*a*	84 15	87 4	87 8
	2	79 14	2*a*	84 20	87 3	
	3	79 28	3*a*	84 12	87 16	
Na	1	78 34	1*a*	84 12	86 44	86 48
	2	78 44	2*a*	84 17	86 47	
	3	78 46	3*a*	84 5	86 54	
Tl.........	1	78 0	1*a*	84 9	86 24	86 32
	2	78 14	2*a*	84 9	86 33	
	3	78 13	3*a*	83 55	86 40	

Measurements of $2H_a$ and $2H_o$ were only possible as far as the green of the spectrum, on account of the large absorption by these red crystals, thick plates being required in order to yield clear interference figures.

Dispersion of the Median Lines.—This was determined by immersion of the section-plates perpendicular to the first median line in oil of cloves, the refractive index of which for sodium light, 1·5409 (re-determined at the time), is practically identical with that (mean of all three indices, 1·5402) of the crystals. It was found that the median lines are dispersed 10′ in the symmetry plane, so that for green thallium light the first median line is nearer to the inclined axis a by 10′ than for red C-light.

Refractive Indices.—Results with six 60°-prisms, each ground to afford two indices directly.

Refractive Indices of Cæsium Cobalt Selenate.

Light.	α.	β.	γ.
Li................	1·5316	1·5360	1·5412
C	1·5321	1·5365	1·5418
Na	1·5354	1·5399	1·5453
Tl	1·5389	1·5434	1·5489
Cd	1·5409	1·5454	1·5510
F	1·5430	1·5475	1·5531
G	1·5492	1·5539	1·5596

Mean of α, β, and γ for Na light = 1·5402.

α = Vibration direction parallel to second median line, 19° 23′ in front of axis c.

β = ,, ,, ,, symmetry axis b.

γ = ,, ,, ,, first median line, 3° 5′ below axis a.

Double refraction, $\mathrm{Na}_{\gamma-\alpha} = 0{\cdot}0099$.

General formula for the intermediate refractive index β, corrected to a vacuum (correction + 0·0004) :—

$$\beta = 1{\cdot}5205 + \frac{784\ 570}{\lambda^2} - \frac{3\ 376\ 600\ 000\ 000}{\lambda^4} + \dots.$$

The α indices are also reproduced very closely by the formula if the constant 1·5205 be diminished by 0·0045 and the γ indices if the constant be increased by 0·0054.

Observations at 70° C. showed that the refractive indices are diminished by about 0·0018 (varying from 0·0016 to 0·0020) for 60° rise of temperature.

Axial Ratios of the Optical Ellipsoid—

$\alpha : \beta : \gamma = 0{\cdot}9971 : 1 : 1{\cdot}0035$, $\mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0029 : 1 : 0{\cdot}9965$.

Molecular Optical Constants.

	Axis of optical indicatrix.		α.	β.	γ.
Lorenz ……	Specific refraction, $\frac{n^2-1}{(n^2+2)d} = \mathfrak{n}$ ………	C	0·1002	0·1009	0·1017
		G	0·1028	0·1036	0·1044
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$…	C	71·51	72·00	72·59
		G	73·41	73·93	74·56
	Specific dispersion. $\mathfrak{n}_G - \mathfrak{n}_C$ …………………		0·0026	0·0027	0·0027
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$ ……………		1·90	1·93	1·97
Gladstone…	Molecular refraction, $\frac{n-1}{d}$ M ……………	C	122·77	123·79	125·01

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha+\beta+\gamma) = 123{\cdot}86$.

Ammonium Cobalt Selenate $(NH_4)_2Co(SeO_4)_2 . 6H_2O$.

Crystal System.—Monoclinic. Class No. 5, holohedral-prismatic.

Axial Angle.—$\beta = 106^\circ\ 23'$. The same value was found by Topsøe.

Ratio of Axes.—$a : b : c = 0{\cdot}7449 : 1 : 0{\cdot}5031$.

Topsøe's values $0{\cdot}7414 : 1 : 0{\cdot}5037$.

Forms observed.—$b\{010\}$, $c\{001\}$, $p\{110\}$, $p'\{120\}$, $q\{011\}$, $m\{021\}$, $o'\{\bar{1}11\}$, $r'\{\bar{2}01\}$.

The forms $p'\{120\}$ and $m\{021\}$ were not observed by Topsøe.

Habit.—More or less tabular parallel to $c\{001\}$, but with the $q\{011\}$ faces also considerably developed. A typical crystal is represented in Fig. 7.

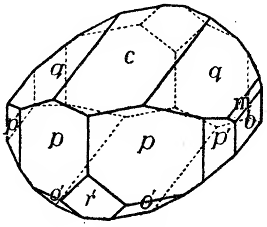

Fig. 7.

The type is thus intermediate between that of the potassium salt shown in fig. 1 and that of the cæsium salt represented in fig. 5. It is not unlike that of the rubidium salt (fig. 3), but the faces of $q\{011\}$ and $r'\{\bar{2}01\}$ were generally larger. The relative importance of the subsidiary faces was generally more or less as shown in fig. 7. Some excellent little faces of $p'\{120\}$ were observed, affording sharp signal images. One good little face of the very rare clinodomal form $m\{021\}$ was discovered on one of the twelve crystals measured, which belonged to three different crops of particularly good crystals. Some relatively large and excellently reflecting faces of the clinopinakoid $b\{010\}$ were present on the crystals of certain crops.

Interfacial Angles of Ammonium Cobalt Selenate.

Angle.	No. of measurements.	Limits.	Mean observed.	Calculated.	Diff.	Topsøe's values.
		° ′ ° ′	° ′	° ′	′	° ′
ac = (100) : (001)...	—	—	—	73 37	—	
as = (100) : (101)...	—	—	—	45 3	—	
sc = (101) : (001)...	—	—	—	28 34	—	
cr′ = (001) : $(\bar{2}01)$...	21	64 15– 64 51	64 35	64 30	5	64 58
cs′ = (001) : $(\bar{1}01)$...	—	—	—	38 42	—	
s′r′ = $(\bar{1}01)$: $(\bar{2}01)$...	—	—	—	25 48	—	
r′a = $(\bar{2}01)$: $(\bar{1}00)$...	—	—	—	41 53	—	
r′c = $(\bar{2}01)$: $(00\bar{1})$...	21	115 12–115 45	115 25	115 30	5	
ap = (100) : (110)...	—	—	—	35 32	—	
pp′ = (110) : (120)...	12	19 22– 19 31	19 27	19 28	1	
p′b = (120) : (010)...	11	34 55– 35 7	35 2	35 0	2	
pp‴ = (110) : (130)...	—	—	—	29 27	—	
p‴b = (130) : (010)...	—	—	—	25 1	—	
pb = (110) : (010)...	48	54 16– 54 49	54 28	*	—	54 35
pp = (110) : $(1\bar{1}0)$...	25	70 50– 71 18	71 3	71 4	1	70 51
cq = (001) : (011)...	41	25 41– 25 57	25 46	*	—	25 41
qm = (011) : (021)...	1	—	18 16	18 14	2	
mb = (021) : (010)...	1	—	45 56	46 0	4	
qb = (011) : (010)...	42	64 4– 64 22	64 14	64 14	0	64 17
ao = (100) : (111)...	—	—	—	48 17	—	
oq = (111) : (011)...	—	—	—	27 0	—	
aq = (100) : (011)...	—	—	—	75 17	—	
qo′ = (011) : $(\bar{1}11)$...	—	—	—	34 50	—	
o′a = $(\bar{1}11)$: $(\bar{1}00)$...	—	—	—	69 53	—	
co = (001) : (111)...	—	—	—	34 10	—	
op = (111) : (110)...	—	—	—	42 34	—	
cp = (001) : (110)...	40	76 35– 76 52	76 44	*	—	76 43
po′ = (110) : $(11\bar{1})$...	14	58 2– 58 38	58 18	58 19	1	
o′c = $(11\bar{1})$: $(00\bar{1})$...	14	44 41– 45 17	44 56	44 57	1	
pc = (110) : $(00\bar{1})$...	40	103 10–103 23	103 16	103 16	0	103 17
bn = (010) : (121)...	—	—	—	54 33	—	
no = (121) : (111)...	—	—	—	15 51	—	
bo = (010) : (111)...	—	—	—	70 24	—	
os = (111) : (101)...	—	—	—	19 36	—	
bo′ = (010) : $(\bar{1}11)$...	7	65 5– 65 10	65 7	65 3	4	
o′s′ = $(\bar{1}11)$: $(\bar{1}01)$...	—	—	—	24 57	—	
o′o′ = $(\bar{1}11)$: $(\bar{1}\bar{1}1)$...	4	49 45– 49 50	49 48	49 54	6	
sq = (101) : (011)...	—	—	—	37 44	—	
qp = (011) : $(\bar{1}10)$...	40	87 17– 87 34	87 24	87 22	2	87 26
ps = $(\bar{1}10)$: $(\bar{1}0\bar{1})$...	—	—	—	54 54	—	
pq = $(\bar{1}10)$: $(0\bar{1}\bar{1})$...	40	92 27– 92 47	92 36	92 38	2	
s′q = $(\bar{1}01)$: (011)...	—	—	—	45 21	—	
qn = (011) : (121)...	—	—	—	26 18	—	
np = (121) : (110)...	—	—	—	36 21	—	
qp = (011) : (110)...	40	62 32– 62 53	62 42	62 39	3	62 40
ps′ = (110) : $(10\bar{1})$...	—	—	—	72 0	—	
pq = (110) : $(0\bar{1}\bar{1})$...	40	117 7–117 28	117 18	117 21	3	
r′o′ = $(\bar{2}01)$: $(\bar{1}11)$...	13	35 1– 35 40	35 17	35 17	0	
o′m = $(\bar{1}11)$: (021)...	1	—	36 49	36 41	8	
mp = (021) : (110)...	1	—	55 20	55 20	0	
o′p = $(\bar{1}11)$: (110)...	13	91 46– 92 21	92 5	92 1	4	
pr′ = (110) : $(20\bar{1})$...	38	52 25– 52 45	52 36	52 42	6	52 37
rp = $(\bar{2}01)$: (110)...	38	127 6–127 43	127 24	127 18	6	
Total number of measurements from 12 crystals............	606					

Cleavage.—Perfect parallel $r'\{\bar{2}01\}$. There is also a much less well defined cleavage parallel to $b\{010\}$.

Relative Density.—Six determinations were made by the immersion method.

I.	Density for 19°·2/4°	2·2275	For 20°/4°	2·2273
II.	„ 18°·3/4°	2·2291	„	2·2287
III.	„ 20°·0/4°	2·2279	„	2·2279
IV.	„ 18°·4/4°	2·2287	„	2·2283
V.	„ 18°·6/4°	2·2273	„	2·2270
VI.	„ 18°·6/4°	2·2302	„	2·2299
			Mean	2·2282

Accepted value for 20°/4°......**2·228**.

Molecular Volume.—$\frac{M}{d} = \frac{485{\cdot}93}{2{\cdot}228} = 218{\cdot}10$.

Topsøe obtained the lower value 2·212 for the specific gravity, and consequently also a molecular volume too high, namely, 221·3.

Molecular Distance (topic axial) ratios.—

$$\chi : \psi : \omega = 6{\cdot}3057 : 8{\cdot}4651 : 4{\cdot}2587.$$

Orientation of Optical Ellipsoid.—Plane of optic axes $b\{010\}$. Sign of double refraction, positive. The first median line is the γ axis of the indicatrix, and α is the second median line.

Extinction Direction (2M.L.) in Symmetry Plane.

Plate I......13° 25′, Plate II......14° 35′, Mean......14° 0′,

behind the normal to $c\{001\}$. As the latter is 16° 23′ in front of the vertical axis c, this extinction direction, which is the second median line, lies 2° 23′ in front of the vertical axis c. The first median line lies 14° 0′ above the inclined axis a. Topsøe obtained 2° 41′ and 13° 42′ for these two extinction angles. These facts are graphically illustrated in fig. 8.

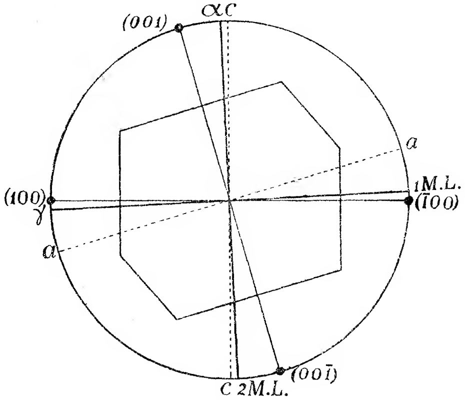

Fig. 8.

Optic Axial Angle.—This is so large that 2E, the angle in air, is indeterminable. Results for $2H_a$, $2H_o$, and the true angle $2V_a$, from three pairs of plates, ground perpendicular to the two bisectrices, are given below. One pair of them were measurable as far as the green of cadmium, the other two pairs only as far as thallium green; beyond these spectrum limits the absorption by these red plates was too great, as thick plates are required to give sharp interference figures.

Ammonium Cobalt Selenate.

Determination of True Optic Axial Angle in Bromonaphthalene.

Light.	No. of plate perp. 1 M.L.	Observed $2H_a$.	No. of plate perp. 2 M.L.	Observed $2H_o$.	Calculated $2V_a$.	Mean $2V_a$.
		° ′		° ′	° ′	° ′
Li	1	74 33	1*a*	88 14	82 3	82 5
	2	74 30	2*a*	88 11	82 2	
	3	74 55	3*a*	88 30	82 9	
C	1	74 32	1*a*	88 10	82 4	82 6
	2	74 29	2*a*	88 7	82 4	
	3	74 53	3*a*	88 25	82 10	
Na	1	74 23	1*a*	87 43	82 12	82 14
	2	74 22	2*a*	87 38	82 14	
	3	74 39	3*a*	87 57	82 16	
Tl	1	74 10	1*a*	87 22	82 16	82 22
	2	74 11	2*a*	87 8	82 23	
	3	74 24	3*a*	87 19	82 26	
Cd	1	—	1*a*	—		
	2	74 5	2*a*	86 50	82 28	82 28
	3	—	3*a*	—		

Topsøe and Christiansen obtained 82° 1′ for $2V_a$, for sodium light.

Dispersion of the Median Lines.—This was determined by immersion in methyl salicylate, the refractive index for sodium light of which, 1·5363, is close to the mean index for that light, 1·5335, for the crystals. The median lines are dispersed 12′ in the symmetry plane, so that the first median line is nearer to the inclined axis *a* for red C light than for green Tl light, by this amount.

Refractive Indices.—The results with the usual six 60°-prisms, each giving two indices, next follow.

Refractive Indices of Ammonium Cobalt Selenate.

Light.	α.	β.	γ.
Li...............	1·5223	1·5287	1·5377
C	1·5228	1·5292	1·5382
Na	1·5261	1·5327	1·5417
Tl...............	1·5294	1·5362	1·5453
Cd	1·5315	1·5380	1·5474
F	1·5335	1·5401	1·5496
G	1·5398	1·5466	1·5562

Mean of α, β, and γ for Na light = 1·5335.

α = Vibration direction parallel to second median line, 2° 23′ in front of vertical axis c.
β = ,, ,, ,, symmetry axis b.
γ = ,, ,, ,, first median line, 14° 0′ above inclined axis a.
Double refraction, $\mathrm{Na}_{\gamma-\alpha} = 0{\cdot}0156$.

General formula for β, corrected to a vacuum :—

$$\beta = 1{\cdot}5116 + \frac{893\ 977}{\lambda^2} - \frac{5\ 122\ 300\ 000\ 000}{\lambda^4} + \ldots.$$

The α indices are equally well reproduced by the formula if the constant 1·5116 be diminished by 0·0066, and the γ indices if it be increased by 0·0090.

Observations at 70° indicated that the refractive indices of ammonium cobalt selenate diminish by about 0·0013 for a rise of temperature of 60°.

Topsøe and Christiansen obtained for β the values 1·5280, 1·5311, and 1·5392 for C, D, and F light respectively; and indirectly for α and γ, for sodium D light only, 1·5244 and 1·5396.

Axial Ratios of the Optical Ellipsoid.—

$$\alpha : \beta : \gamma = 0{\cdot}9957 : 1 : 1{\cdot}0059, \qquad \mathfrak{a} : \mathfrak{b} : \mathfrak{c} = 1{\cdot}0043 : 1 : 0{\cdot}9942.$$

Molecular Optical Constants.

	Axis of optical indicatrix.	α.	β.	γ.
Lorenz	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = \mathfrak{n}$ C	0·1371	0·1385	0·1404
	G	0·1408	0·1423	0·1443
	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathfrak{m}$ ... C	66·60	67·28	68·24
	G	68·41	69·12	70·13
	Specific dispersion, $\mathfrak{n}_G - \mathfrak{n}_C$	0·0037	0·0038	0·0039
	Molecular dispersion, $\mathfrak{m}_G - \mathfrak{m}_C$	1·81	1·84	1·89
Gladstone...	Molecular refraction, $\frac{n-1}{d}$ M C	114·02	115·42	117·38

Mean molecular refraction (Gladstone), $\frac{1}{3}(\alpha+\beta+\gamma)$ = 115·61.

Comparison of Results.

Habit.—The crystals of the potassium, rubidium, and cæsium salts of this cobalt group exhibit the habits which have been observed to be characteristic of these respective salts throughout the series, as so far investigated. They are typified by the relative development of the basal pinakoid *c*{001} and clinodomal prism *q*{011}, the former predominating in the potassium salt and the latter in the cæsium salt, while in the rubidium salt the two forms are more or less equally developed, the habit of this salt being thus very clearly of intermediate character. The crystals of the ammonium salt are usually very much like those of the intermediate rubidium salt, but the limits are wider, the types shown by the potassium and cæsium salts being also each nearly approached in different individuals.

Crystal Elements and Angles.—

Comparison of the Axial Angles and Axial Ratios.

	Axial angle.	Axial ratios.
	β.	$a : b : c$
Potassium cobalt selenate	104° 17′	0·7522 : 1 : 0·5062
Rubidium ,, ,, ...	105° 14′	0·7427 : 1 : 0·5019
Ammonium ,, ,, ...	106° 23′	0·7449 : 1 : 0·5031
Cæsium ,, ,, ...	106° 18′	0·7310 : 1 : 0·4989

From the above Table it will be clear that the monoclinic axial angle β for rubidium cobalt selenate is approximately the mean of the corresponding axial angles for the potassium and cæsium salts. The axial angle of ammonium cobalt selenate is nearly identical with that of cæsium cobalt selenate.

The morphological axial ratios of the rubidium salt are likewise intermediate between the analogous ratios for the potassium and cæsium salts. Thus both as regards the axial angle and the axial ratios the constants follow the order of the atomic weights and atomic numbers of the alkali metals present.

Atomic weights:— K = 38·85, Rb = 84·9, Cs = 131·9.

Atomic numbers:—K = 19, Rb = 37, Cs = 55.

The axial ratios of the ammonium salt are intermediate between the two extremes for the group (for the potassium and cæsium salts), and fairly close to those for the intermediate rubidium salt. True isomorphism of ammonium cobalt selenate with the three alkali-metallic salts of the cobalt group is thus clearly indicated.

Comparison of the Interfacial Angles.

Angle.	KCo selenate.	RbCo selenate.	CsCo selenate.	AmCo selenate.
	° ′	° ′	° ′	° ′
$ac = (100) : (001)$	75 43	74 46	73 42	73 37
$as = (100) : (101)$	46 27	45 48	44 55	45 3
$sc = (101) : (001)$	29 16	28 58	28 47	28 34
$cr' = (001) : (\bar{2}01)$	62 58	63 43	64 46	64 30
$cs' = (001) : (\bar{1}01)$	38 6	38 25	39 0	38 42
$s'r' = (\bar{1}01) : (\bar{2}01)$	24 52	25 18	25 46	25 48
$r'a = (\bar{2}01) : (\bar{1}00)$	41 19	41 31	41 32	41 53
$ap = (100) : (110)$	36 3	35 38	35 4	35 32
$pp' = (110) : (120)$	19 28	19 28	19 28	19 28
$p'b = (120) : (010)$	34 29	34 54	35 28	35 0
$pp''' = (110) : (130)$	29 21	29 26	29 31	29 27
$p'''b = (130) : (010)$	24 36	24 56	25 25	25 1
$pb = (110) : (010)$	53 57	54 22	54 56	54 28
$cq = (001) : (011)$	26 8	25 50	25 35	25 46
$qb = (011) : (010)$	63 52	64 10	64 25	64 14
$ao = (100) : (111)$	49 42	49 0	48 6	48 17
$oq = (111) : (011)$	27 31	27 19	27 14	27 0
$aq = (100) : (011)$	77 13	76 19	75 20	75 17
$qo' = (011) : (\bar{1}11)$	34 15	34 37	35 12	34 50
$o'a = (\bar{1}11) : (\bar{1}00)$	68 32	69 4	69 28	69 53
$co = (001) : (111)$	35 1	34 35	34 14	34 10
$op = (111) : (110)$	43 29	43 5	42 29	42 34
$cp = (001) : (110)$	78 30	77 40	76 43	76 44
$po' = (110) : (11\bar{1})$	57 6	57 42	58 10	58 19
$o'c = (11\bar{1}) : (00\bar{1})$	44 24	44 38	45 7	44 57
$bo = (010) : (111)$	69 51	70 13	70 36	70 24
$os = (111) : (101)$	20 9	19 47	19 24	19 36
$bo' = (010) : (\bar{1}11)$	65 9	65 14	65 17	65 3
$o's' = (\bar{1}11) : (\bar{1}01)$	24 51	24 46	24 43	24 57
$sq = (101) : (011)$	38 27	38 3	37 46	37 44
$qp = (011) : (\bar{1}10)$	85 24	86 28	87 40	87 22
$ps = (\bar{1}10) : (\bar{1}0\bar{1})$	56 9	55 29	54 34	54 54
$s'q = (\bar{1}01) : (011)$	45 3	45 9	45 30	45 21
$qp = (011) : (110)$	64 0	63 30	62 55	62 39
$ps' = (110) : (10\bar{1})$	70 57	71 21	71 35	72 0
$r'o' = (\bar{2}01) : (\bar{1}11)$	34 35	34 49	35 7	35 17
$o'p = (\bar{1}11) : (110)$	92 48	92 40	92 40	92 1
$pr' = (110) : (20\bar{1})$	52 37	52 31	52 13	52 42

From the above comparative Table of 38 measured angles the salient fact is derived that the whole of the angles of the rubidium salt are intermediate between those of the potassium and cæsium salts. The Table is best analysed in the following manner (as for former groups), by working out the average and maximum changes of angle for the various replacements:—

Replacement.	Average change. (Mean change of 38 angles.)	Maximum change.
K by Rb	25′	64′ = 1° 4′
K by Cs	53′	136′ = 2° 16′
K by NH_4	49′	126′ = 2° 6′

The average and maximum changes of angle are thus seen to be twice as great when potassium is replaced by cæsium, as they are when potassium is replaced by rubidium, just as the change of atomic weight or atomic number is twice as great. So that the average change and the maximum change of interfacial angle are directly proportional to the change in atomic weight or atomic number.

The introduction of the radicle ammonium instead of potassium induces an amount of average or maximum change of angle which is just slightly less than when cæsium is substituted for potassium. In the case of 35 of the angles the changes are in the same direction (of same sign) when ammonium is introduced for potassium, as when either rubidium or cæsium is introduced, the only three exceptions being in cases where the change is very minute, not exceeding 6′.

It will be observed that the maximum change of angle for the whole group of four salts is $2\frac{1}{4}°$ (2° 16′), which occurs in the case of one angle, $qp = (011) : (\bar{1}10)$, when potassium in potassium cobalt selenate is replaced by cæsium, or *vice versâ*.

Volume Constants.—

Volume Constants of the Cobalt Group of Double Selenates.

Salt.	Molecular weight.	Specific gravity.	Molecular volume.	Topic axial ratios.
				$\chi : \psi : \omega$
KCo selenate	527 ·77	2 ·530	208 ·60	6 ·2197 : 8 ·2688 : 4 ·1856
RbCo ,, ...	619 ·87	2 ·837	218 ·49	6 ·2901 : 8 ·4693 : 4 ·2508
CsCo ,, ...	713 ·87	3 ·094	230 ·73	6 ·3618 : 8 ·7028 : 4 ·3418
NH_4Co ,, ...	485 ·93	2 ·228	218 ·10	6 ·3057 : 8 ·4651 : 4 ·2587

The density increases with the molecular weight, the changes for the respective replacements of K by Rb and Rb by Cs being as 6 : 5, the effect thus diminishing as the mass grows. The ammonium salt is naturally much the lightest member of the group.

The molecular volume of the three alkali metallic salts increases at an accelerating rate, as the atomic weight or atomic number rises, the amount for the two changes of metal being 9·89 and 12·24 respectively. The molecular volume of ammonium cobalt selenate is almost identical with that of rubidium cobalt selenate, a result as regards the ammonium and rubidium salts always observed so far throughout the series.

The molecular volumes of the double selenates are naturally greater than those of the double sulphates, sulphur and selenium being analogues separated by two whole series of elements in the periodic table, their atomic numbers being 16 and 34; and it is interesting to see what is the amount of the increase in the molecular volume on replacing sulphur by selenium. As there are two atoms of sulphur or selenium in the molecule of the double salt, we obtain the increase *per* atom by subtracting the molecular volume of the double sulphate from that of the double selenate and dividing by two. The results of doing this, for the analogous salts of all the five pairs of groups of monoclinic double salts yet completely investigated, are given in the next Table. The results also for the simple sulphates and selenates are added for comparison, and in this case, as there is only one atom of sulphur or selenium in the simple rhombic salt, there is no division by two, the differences of molecular volume for the analogous sulphate and selenate giving the increase *per* atom directly. Only the strictly analogous potassium, rubidium, and cæsium salts are compared throughout; for no comparable value can be got for the simple ammonium salts, as ammonium selenate crystals are only available for molecular volume determinations in the monoclinic and not the rhombic form.

Increase of Molecular Volume on Replacing S by Se.

Salt group.	Increase per atom.
Cobalt	6·3 to 6·7 units.
Iron	6·2 ,,
Nickel	6·1 to 6·8 ,,
Magnesium	6·0 to 6·1 ,,
Zinc	6·3 to 6·4 ,,
Simple salts of alkalies	6·5 to 6·8 ,,

The replacement of one atom of sulphur by an atom of selenium is thus found to be accompanied by an increase of 6·0 to 6·8 units of molecular volume. The results are very similar and concordant for the various groups of salts, both double and single.

The molecular distance (topic axial) ratios of the rubidium salt are also intermediate between those for the potassium and cæsium salts, the axial or edge dimensions of the monoclinic elementary cell of the space-lattice increasing progressively with the atomic weight or atomic number of the alkali metal. These constants for the ammonium salt are almost identical with those for the rubidium salt, two of the three dimensions being very slightly greater, and the third a minute amount less. The space-lattice cells of the rubidium and ammonium salts are thus practically congruent or coincident.

Cleavage.—There is a perfect cleavage parallel to the orthopinakoid $r'\{\bar{2}01\}$ in the crystals of all four salts. This is the common cleavage direction of the whole series of double sulphates, and of all the groups of the double selenates yet studied, belonging to this same monoclinic isomorphous series crystallising with $6H_2O$. In addition, a feeble facility for cleavage has also been observed in ammonium cobalt selenate parallel to the clinopinakoid $b\{010\}$. Ammonium nickel selenate was also found to exhibit this same second cleavage direction, as also four of the ammonium double sulphates, those of the magnesium, nickel, manganese, and copper groups.

Orientation of Optical Ellipsoid.—The symmetry requires only one of the three rectangular axes of the optical ellipsoid to be fixed, namely, that which is identical with the symmetry axis *b*. The two others, lying in the symmetry plane, may be anywhere in that plane consistent with their mutual rectangularity. They are not only differently situated for the different salts, but even for the same salt they are dispersed slightly for different wave-lengths of light.

The position of the ellipsoid is thus conveniently determined by giving the position for a specific wave-length of that one of the two latter axes which is not far removed from the vertical crystal axis *c*; it is the α axis of the indicatrix and the second median line for all four salts.

Inclination of α Axis of Indicatrix to Vertical Axis *c*, in front, for Na Light.

NH_4Co selenate	2° 23′
KCo ,,	8° 54′
RbCo ,,	12° 50′
CsCo ,,	19° 23′

The Table indicates that the ellipsoid is so situated that in the crystals of the ammonium salts its α axis lies very near, and just in front of, the vertical crystal axis *c*. In the crystals of the salts containing the three alkali metals it is situated so that this axis α is further and further removed from the vertical axis as the atomic weight or atomic number of the alkali metal increases. The ellipsoid thus rotates about the symmetry axis *b* when one alkali metal is exchanged for another, and progressively at an accelerating rate, following the ascending order of the atomic weights or atomic numbers of the interchanged metals. Its position for each of the four salts is graphically indicated in fig. 9, which shows the progression clearly.

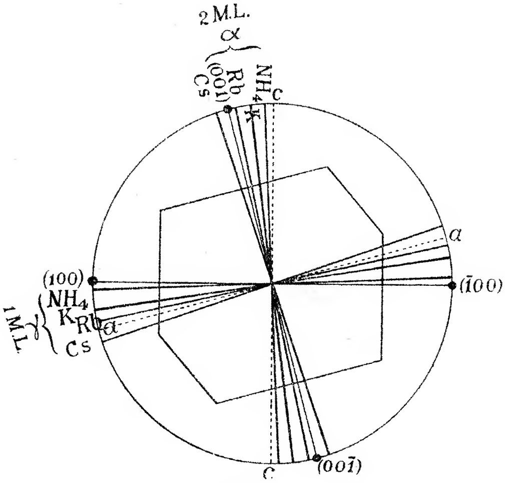

FIG. 9.

Optic Axial Angles.—The plane of symmetry *b*{010} is the common plane of the optic axes for the whole group. In all four cases the sign of the double refraction is positive, and the first median line is the γ axis of the indicatrix lying in the symmetry plane not far removed from the inclined crystal axis *a*.

Optic Axial Angles $2V_a$ of the Cobalt Group of Double Selenates.

	KCo selenate.	RbCo selenate.	AmCo selenate.	CsCo selenate.
Li....................	62° 12′	73° 42′	82° 5′	87° 11′
C....................	62 13	73 41	82 6	87 8
Na....................	62 19	73 37	82 14	86 48
Tl....................	62 27	73 33	82 22	86 32
Cd....................	—	—	82 28	—

The optic axial angle is thus seen to increase with the atomic weight or atomic number of the alkali metal, the value for the rubidium salt being intermediate, slightly nearer to that of the potassium salt. The optic axial angle of ammonium cobalt selenate comes between those for the rubidium and cæsium salts.

Refractive Indices.—

Comparison of the Refractive Indices.

Index.	Light.	KCo selenate.	RbCo selenate.	NH_4Co selenate.	CsCo selenate.
α	Li	1·5122	1·5163	1·5223	1·5316
	C	1·5127	1·5168	1·5228	1·5321
	Na	1·5158	1·5199	1·5261	1·5354
	Tl	1·5190	1·5232	1·5294	1·5389
	Cd	1·5211	1·5252	1·5315	1·5409
	F	1·5231	1·5273	1·5335	1·5430
	G	1·5293	1·5333	1·5398	1·5492
β	Li	1·5181	1·5220	1·5287	1·5360
	C	1·5186	1·5225	1·5292	1·5365
	Na	1·5218	1·5256	1·5327	1·5399
	Tl	1·5250	1·5290	1·5362	1·5434
	Cd	1·5271	1·5311	1·5380	1·5454
	F	1·5291	1·5332	1·5401	1·5475
	G	1·5354	1·5393	1·5466	1·5539
γ	Li	1·5341	1·5329	1·5377	1·5412
	C	1·5347	1·5334	1·5382	1·5418
	Na	1·5380	1·5369	1·5417	1·5453
	Tl	1·5415	1·5404	1·5453	1·5489
	Cd	1·5435	1·5425	1·5474	1·5510
	F	1·5456	1·5446	1·5496	1·5531
	G	1·5522	1·5508	1·5562	1·5596
Mean refractive index $\frac{1}{3}(\alpha + \beta + \gamma)$ for Na light		1·5252	1·5275	1·5335	1·5402
Double refraction, $Na_{\gamma-\alpha}$		0·0222	0·0170	0·0156	0·0099

The α and β indices of the rubidium salt will be observed to be intermediate between the corresponding indices for the potassium and cæsium salts. As, however, a great diminution of double refraction $(\gamma-\alpha)$ for Na light occurs as the atomic weight or atomic number rises, the γ indices for the rubidium salt are slightly less than those of the potassium salt. The mean refractive index, however, for the rubidium salt is intermediate between the mean indices of the potassium and cæsium salts. The effect of change of double refraction is overcome at the cæsium salt, as the change in refractive index is a more considerably accelerating one, so that all the cæsium salt indices indicate an advance in refractive power.

The refractive indices of the ammonium salt are intermediate between those of the rubidium and cæsium salts.

Double Refraction.—The progression, a diminution, with rise in atomic number or atomic weight, already alluded to, will be clearly apparent from the last line of the Table. The value for the ammonium salt is just beyond that for the rubidium salt.

Axial Ratios of Optical Indicatrix.—Similar facts are expressed by these ratios of the axes of the indicatrix, which are directly proportional to the refractive indices. The slight set-back of the γ value for the rubidium salt, due to the operation of the fall in double refraction, is shown by the second right-hand series of ratios, for all of which the β value of the potassium salt is taken as unity. This right-hand series of ratios expresses the total change in the dimensions of the optical ellipsoid on passing from one salt to the other, just as the Table for the inclination of the α axis of the ellipsoid to the vertical crystal axis indicates the position of the ellipsoid in the various salts, the two Tables together thus giving complete information concerning the dimensions and orientation of the optical ellipsoid in the crystal.

Axial Ratios of the Optical Indicatrix.

	$\alpha : \beta : \gamma$	$\alpha : \beta : \gamma$
KCo selenate	0·9960 : 1 : 1·0106	0·9960 : 1 : 1·0106
RbCo ,, ...	0·9963 : 1 : 1·0074	0·9988 : 1·0025 : 1·0099
NH_4Co ,, ...	0·9957 : 1 : 1·0059	1·0028 : 1·0072 : 1·0131
CsCo ,, ...	0·9971 : 1 : 1·0035	1·0089 : 1·0119 : 1·0154

Molecular Optical Constants.—

Specific Refraction and Dispersion (Lorenz).

Selenate.	Specific refraction, $\frac{n^2-1}{(n^2+2)\,d} = \mathrm{n}$.						Specific dispersion. $\mathrm{n}_G - \mathrm{n}_C$.		
	For ray C(Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
AmCo ...	0·1371	0·1385	0·1404	0·1408	0·1423	0·1443	0·0037	0·0038	0·0039
KCo	0·1187	0·1199	0·1230	0·1220	0·1231	0·1263	0·0033	0·0032	9·0033
RbCo ...	0·1066	0·1076	0·1095	0·1094	0·1105	0·1124	0·0028	0·0029	0·0029
CsCo	0·1002	0·1009	0·1017	0·1028	0·1036	0·1044	0·0026	0·0027	0·0027

Molecular Refraction and Dispersion (Lorenz).

Selenate.	Molecular refraction, $\frac{n^2-1}{n^2+2} \cdot \frac{M}{d} = \mathrm{m}$.						Molecular dispersion. $\mathrm{m}_G - \mathrm{m}_C$.		
	For ray C (Hα).			For ray Hγ near G.					
	α.	β.	γ.	α.	β.	γ.	α.	β.	γ.
KCo.....................	62·66	63·27	64·91	64·36	64·98	66·68	1·70	1·71	1·77
RbCo	66·08	66·69	67·86	67·84	68·48	69·69	1·76	1·79	1·83
AmCo	66·60	67·28	68·24	68·41	69·12	70·13	1·81	1·84	1·89
CsCo	71·51	72·00	72·59	73·41	73·93	74·56	1·90	1·93	1·97

Molecular Refraction (Gladstone and Dale).

Selenate.	$\frac{n-1}{d}M$ for ray C.			Mean molecular refraction for ray C. $\frac{1}{3}(\alpha+\beta+\gamma)$.
	α.	β.	γ.	
KCo	106·95	108·18	111·54	108·89
RbCo	112·92	114·16	116·54	114·54
AmCo	114·02	115·42	117·38	115·61
CsCo	122·77	123·79	125·01	123·86

The whole of the specific and molecular optical constants of the rubidium salt given in the above Tables are intermediate between those of the potassium and cæsium salts. The molecular refraction increases considerably more when cæsium replaces rubidium than when the latter replaces potassium, the proportion being as 5 : 3. The increases are nearly alike along the α and β axes, but are less along the γ axis. These conclusions are independent of the temperature within ordinary limits, as it was directly proved that the refractive indices of all the salts were lowered by raising the temperature, which is the same direction of change as the density suffers on rise of temperature; so that the effect of temperature is similar on both the numerator and denominator factors involved in the calculation of molecular refraction.

The molecular refraction of ammonium cobalt selenate is very close to (slightly higher than) that for rubidium cobalt selenate, a result in keeping with that derived from a comparison of the morphological constants, the topic axial ratios.

A comparison of the values for the molecular refraction of these four cobalt double selenates with the analogous values for the four cobalt double sulphates shows that the selenate values are higher by 7·0 to 8·2 Lorenz units, or 13·0 to 14·2 Gladstone units. Dividing by two for the number of atoms present, this gives 3·5 to 4·1 Lorentz units, or 6·5 to 7·1 Gladstone units, for the increase per atom, when sulphur is replaced by selenium. This accords well with the similar results derived from the other groups already studied, as recorded in the following final Table :—

Increase of Molecular Refraction on Replacing S by Se.

Salt group.	Lorenz units.	Gladstone units.
Cobalt	3·5–4·1	6·5–7·1
Iron	3·5–4·0	6·4–7·1
Nickel	3·5–4·0	6·3–7·2
Magnesium	3·4–3·6	6·3–6·7
Zinc	3·5–3·7	6·5–6·9
Simple salts of alkalies	3·4–3·8	6·2–7·2

Concluding Remarks.

The foregoing results are in complete accord with those derived from the study of four other groups (the zinc, magnesium, nickel, and iron groups) of double selenates previously described, and from the fully completed investigation of all the eight known groups of the analogous double sulphates, all belonging to this grandly crystallising monoclinic isomorphous series, $R_2M\left(\begin{smallmatrix}S\\Se\end{smallmatrix}O_4\right)_2.6H_2O$. The dominating facts revealed are again (1) the progressive character of all the crystallographic and physical properties, following the progression of the atomic numbers (and therefore atomic weights) of the interchangeable and predominatingly determinative alkali metals concerned, potassium, rubidium, and cæsium; and (2) the almost perfect isostructure, that is, congruency, coincidence, and equality of dimensions of the elementary cells of the monoclinic space-lattices, of the crystals of the ammonium and rubidium salts of the group.

A natural and logical explanation of the progression referred to in result (1) is afforded by Moseley's law, as was explained in detail at the conclusion of the memoir concerning the nickel group.* Still more recent work on the structure of the atom has only the more confirmed and amplified the explanation. It is, undoubtedly, the progression in the complexity of the structure of the atoms of the alkali metals, with all its physical and chemical consequences, that causes the progressive modification in the morphology and physical properties of the crystals of these double salts in which they play so dominant a part.

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* *Loc. cit.*, p. 234.